

CLAIMS

1. A process, comprising:
  - providing a reaction medium comprising:
    - a protic solution;
    - a photocatalyst capable of a two electron reduction of hydrogen ions; and
    - a coproduct trap;
  - exposing the reaction medium to radiation capable of photoexciting the photocatalyst to produce hydrogen.
2. The process of claim 1, wherein the protic solution comprises at least one of hydrohalic acid, a silane, and water.
3. The process of claim 2, wherein the hydrohalic acid is selected from hydrochloric acid, hydrogen bromide, hydrogen fluoride and hydrogen iodide.
4. The process of claim 1, wherein the coproduct trap comprises at least one of tetrahydrofuran, silane, isopropanal, dihydroanthracene and 2,3 dimethylbutadiene.
5. The process of claim 1, wherein the photocatalyst capable of a two electron reduction of hydrogen ions comprises a multinuclear transition metal core.
6. The process of claim 5, wherein the multinuclear transition metal core comprises at least one of rhodium, iridium, platinum and palladium.
7. The process of claim 6, wherein the catalyst capable of a two electron reduction of hydrogen ions further comprises at least one of triphenyl phosphine, carbon

monoxide, bis(difluorophosphino)methyl amine, MeCN, a phosphazene based ligand and a two electron donor ligand.

8. The process of claim 1, wherein the catalyst capable of a two electron reduction of hydrogen ions comprises:
  - a binuclear transition metal core; and
  - ligands capable of stabilizing a two electron mixed valence state of the binuclear transition metal core.
9. The process of claim 8, wherein the ligands comprise:
  - at least two  $\pi$ -acid groups capable of coordinating with the binuclear transition metal core; and
  - at least one Lewis basic atom or group.
10. The process of claim 8, wherein the ligands comprise:
  - at least two  $\pi$ -donating groups capable of coordinating with the binuclear transition metal core; and
  - at least one Lewis acidic atom or group.
11. The process of claim 9, wherein the ligands comprise a phosphazane group.
12. The process of claim 11, wherein the ligands comprise a group capable of giving at least one phosphorous atom of the phosphazane group strong  $\pi$ -acid characteristics.
13. The process of claim 12, wherein the group capable of giving one phosphorous atom strong  $\pi$ -acid characteristics comprises at least one of halogen, fluorine, chlorine, halogenated alkanes, halogenated alkenes, aryl substituted with electron withdrawing groups, and alcohols.

14. The process of claim 11, wherein the ligand comprises a group attached to a nitrogen atom of the phosphazane group which allows participation of a lone pair of electrons to participate in  $\pi$ -bonding.
15. The process of claim 14, wherein the group attached to a nitrogen atom comprises at least one of substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl groups, methyl, ethyl, propyl, butyl, pentyl, hydrogen and a substituted phenyl, wherein the alkyl group is selected from branched and unbranched alkyl groups.
16. The process of claim 10, wherein the ligand comprises a boron bonded to two nitrogen atoms.
17. A process, comprising:
- providing a reaction medium comprising:
- a protic solution;
- a photocatalyst comprising a binuclear transition metal complex and a ligand capable of supporting the photocatalyst in a two electron mixed valence state; and
- a coproduct trap; and
- photoexciting the photocatalyst to produce hydrogen and eliminate halogen atoms.
18. The process of claim 17, wherein the ligand is a diphosphazane ligand.
19. The process of claim 18, wherein the ligand has strongly  $\pi$ -acidic phosphine group.
20. The process of claim 17, wherein the binuclear transition metal complex comprises at least one of rhodium and iridium.

21. A process, comprising:
- exciting at least two photocatalysts to an active state, wherein the photocatalysts comprises two rhodium atoms;
- contacting the photocatalysts with hydrogen ions and halogen ions of a hydrohalic acid solution, thereby producing hydrogen and a photocatalyst in a mixed valence state comprising halogen atoms; and
- irradiating the photocatalyst in a mixed valence state to eliminate at least a portion of the halogen atoms.
22. The process of claim 21, wherein at least one photocatalyst comprises carbon monoxide; and exciting the photocatalyst comprising photoexciting the photocatalyst to liberate the carbon monoxide.
23. The process of claim 21, wherein a hydrogen ion and a halogen ion bind to the photocatalysts prior to reacting to form hydrogen and a photocatalytic intermediate.
24. The process of claim 23, wherein the photocatalyst intermediate reacts with additional hydrogen ions and halogen ions to form a photocatalyst comprising four halogen atoms, and hydrogen.
25. The process of claim 21, further comprising:
- consuming the halogen atoms in a halogen-atom trap.
26. The process of claim 21, further comprising:
- irradiating the photocatalyst with sufficient energy to regenerate the photocatalyst in an active state.

27. The process of claim 21, wherein irradiating the photocatalyst comprises exposing the photocatalyst to visible light.
28. A process, comprising:
- irradiating a transition metal complex comprising:
- two rhodium atoms,
- three bis(difluorophosphine) methyl amine ligands, and
- triphenyl phosphine;
- in a solution comprising hydrohalic acid and a halogen trap.
29. The process of claim 28, wherein hydrogen is produced.
30. The process of claim 29, wherein the halogen trap comprises at least one of tetrahydrofuran, dihydroanthracene, silane and 2,3 dimethylbutadiene.
31. A compound, comprising:
- two transition metal atoms, wherein the transition metal atoms are in a two electron mixed valence state and at least one transition metal is not rhodium; and
- at least one ligand capable of stabilizing the transition metal atom in a two electron mixed valence state.
32. The compound of claim 31, wherein the ligand is a diphosphazane ligand.
33. The compound of claim 32, wherein the ligand has strongly  $\pi$ -acidic phosphine group.
34. The compound of claim 31, comprising at least two the ligands are capable of stabilizing a two electron mixed valence state of the two iridium atoms.
35. The compound of claim 34, wherein the ligands comprise:

at least two  $\pi$ -acid groups capable of coordinating with the binuclear transition metal core; and

at least one Lewis basic atom or group.

36. The compound of claim 34, wherein the ligands comprise:

at least two  $\pi$ -donating groups capable of coordinating with the binuclear transition metal core; and

at least one Lewis acidic atom or group.

37. The compound of claim 34, comprising at least three ligands capable of stabilizing a two electron mixed valence state of the two iridium atoms.

38. The compound of claim 37, wherein the ligands comprise a diphosphazane group.

39. The compound of claim 38, wherein the ligand is bis(difluorophosphine)methyl amine.

40. The process of claim 38, wherein the ligands comprise a group capable of giving at least one phosphorous atom of the phosphazane group strong  $\pi$ -acid characteristics.

41. The process of claim 35, wherein the group capable of giving one phosphorous atom strong  $\pi$ -acid characteristics comprises at least one of halogen, fluorine, chlorine, halogenated alkanes, halogenated alkenes, aryl substituted with electron withdrawing groups, and alcohols.

42. The process of claim 38, wherein the ligand comprises a group attached to a nitrogen atom of the phosphazane group which allows participation of a lone pair of electrons to participate in  $\pi$ -bonding.

43. The process of claim 42, wherein the group attached to a nitrogen atom comprises at least one of substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl groups, methyl, ethyl, propyl, butyl, pentyl, hydrogen and a substituted phenyl, wherein the alkyl group is selected from branched and unbranched alkyl groups.
44. The process of claim 31, wherein the ligand comprises a boron bonded to two nitrogen atoms.
45. A process, comprising:
- providing a reaction medium comprising:
- a protic solution;
- a photocatalyst capable of a two electron reduction of hydrogen ions, wherein the photocatalyst comprises:
- a binuclear transition metal core; and
- at least one chelating ligand coordinated to one transition metal of the binuclear transition metal core; and
- a coproduct trap;
- exposing the reaction medium to radiation capable of photoexciting the photocatalyst to produce hydrogen.
46. The process of claim 45, wherein the protic solution comprises at least one of hydrohalic acid, a silane, and water.
47. The process of claim 46, wherein the hydrohalic acid is selected from hydrochloric acid, hydrogen bromide, hydrogen fluoride and hydrogen iodide.

48. The process of claim 45, wherein the coproduct trap comprises at least one of tetrahydrofuran, silane, isopropanal, dihydroanthracene and 2,3 dimethylbutadiene.
49. The process of claim 45, wherein the photocatalyst capable of a two electron reduction of hydrogen ions comprises a multinuclear transition metal core.
50. The process of claim 49, wherein the multinuclear transition metal core comprises at least one of rhodium, iridium, platinum and palladium.
51. The process of claim 50, wherein the catalyst capable of a two electron reduction of hydrogen ions further comprises at least one of triphenyl phosphine, carbon monoxide, bis(difluorophosphino)methyl amine, MeCN, a phosphazene based ligand and a two electron donor ligand.
52. The process of claim 45, wherein the catalyst capable of a two electron reduction of hydrogen ions comprises:
- a binuclear transition metal core; and
  - ligands capable of stabilizing a two electron mixed valence state of the binuclear transition metal core.
53. The process of claim 52, wherein the ligands comprise:
- at least two  $\pi$ -acid groups capable of coordinating with the binuclear transition metal core; and
  - at least one Lewis basic atom or group.
54. The process of claim 52, wherein the ligands comprise:
- at least two  $\pi$ -donating groups capable of coordinating with the binuclear transition metal core; and

at least one Lewis acidic atom or group.

55. The process of claim 53, wherein the ligands comprise a phosphazane group.
56. The process of claim 55, wherein the ligands comprise a group capable of giving at least one phosphorous atom of the phosphazane group strong  $\pi$ -acid characteristics.
57. The process of claim 56, wherein the group capable of giving one phosphorous atom strong  $\pi$ -acid characteristics comprises at least one of halogen, fluorine, chlorine, halogenated alkanes, halogenated alkenes, aryl substituted with electron withdrawing groups, and alcohols.
58. The process of claim 55, wherein the ligand comprises a group attached to a nitrogen atom of the phosphazane group which allows participation of a lone pair of electrons to participate in  $\pi$ -bonding.
59. The process of claim 58, wherein the group attached to a nitrogen atom comprises at least one of substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl groups, methyl, ethyl, propyl, butyl, pentyl, hydrogen and a substituted phenyl, wherein the alkyl group is selected from branched and unbranched alkyl groups.
60. The process of claim 54, wherein the ligand comprises a boron bonded to two nitrogen atoms.
61. The process of claim 45, wherein the photocatalyst is in two electron mixed valence state and the photocatalyst further comprises:  
two charged ligands coordinated to the transition metal in the higher oxidation state.
62. The process of claim 61, wherein at least one chelating ligand is coordinated to

the transition metal in the lower oxidation state.

63. The process of claim 61, further comprising:

exposing the reaction medium to radiation capable of photoexciting the photocatalyst to produce hydrogen, further comprises:  
forming of a photocatalyst to a valence-symmetric state; and  
rearranging the chelating ligand to coordinate with both transition metals of the binuclear core.

64. The process of claim 61, wherein the protic solution is a hydrohalic acid and the photocatalyst in a valence-symmetric state comprises four halogen atoms.

65. The process of claim 64, further comprising:

photoexciting the photocatalyst in a valence-symmetric state to eliminate two of the halogen atoms and regenerate the photocatalyst capable of a two electron reduction of hydrogen ions.